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Impact of reactive bromine chemistry in the troposphere

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Abstract

Recently several field campaigns and satellite observations found strong indications for bromine oxide (BrO) in the free troposphere. Using a global atmospheric chemistry transport model we show that BrO measurements mixing ratios of a few tenths to 2 pmol mol^{-1} lead to a reduction in the zonal mean O_3 mixing ratio of up to 18% in widespread areas and locally even up to 40% compared to a model run without bromine chemistry. For dimethyl sulfide (DMS) the effect is even larger with up to 60% decreases. This is accompanied by dramatic changes in DMS oxidation pathways, reducing its cooling effect on climate. Changes in the HO_2:OH ratio also cause changes for NO_x and PAN. These results imply that a very strong sink for O_3 and DMS has so far been ignored in many studies of the chemistry of the troposphere.

1. Introduction

In the last two decades reactive halogens have been identified as important reactants in the troposphere (see e.g. von Glasow and Crutzen, 2003, for an overview). BrO has been found in the boundary layer during polar ozone depletion events (ODEs) (Hausmann and Platt, 1994), over salt lakes (Hebestreit et al., 1999; Stutz et al., 2002; Hönninger et al., 2004), and in the marine boundary layer (MBL) (Leser et al., 2003; Saiz-Lopez et al., 2004) and also in volcanic plumes (Bobrowski et al. (2003), N. Bobrowski, pers. comm.). Satellite observations showed the widespread presence of BrO in the troposphere outside the polar regions (Wagner and Platt, 1998; Pundt et al., 2000; Fitzenberger et al., 2000; Wagner et al., 2001; Van Roozendael et al., 2002; Richter et al., 2002; Hollwedel et al., 2004) with global background vertical columns of about $1–3\times10^{13}$ molec cm^{-2}, corresponding to BrO mixing ratios of 0.5–2 pmol mol^{-1} if uniformly mixed in the troposphere. Comparisons with balloon and ground measurements in mid and high northern latitudes (between 42 and 68° N, Harder et al., 1998; Fitzenberger et al., 2000; Van Roozendael et al., 2002) as well as the diurnal variation

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of ground based BrO column measurements (Van Roozendael et al., 2002) indicated that the tropospheric BrO was mainly located within the free troposphere (FT). Further evidence for free tropospheric BrO in high latitudes comes from high-altitude aircraft observations in the Arctic by McElroy et al. (1999). Such observations have not been made yet at lower latitudes. Although most evidence indicates that the measured BrO is located in the FT, these data do not exclude contributions from the MBL. Ongoing work is estimating tropospheric vertical columns of BrO from satellite data but it is expected to yield reliable data only in the polar regions or other regions of strongly elevated BrO (J. Hollwedel, pers. comm.).

Halogens affect ozone by directly destroying it and by reducing its production. The main destruction cycle is:

$$O_3 + Br \longrightarrow BrO + O_2 \qquad (Br1)$$

$$BrO + HO_2 \longrightarrow HOBr + O_2 \qquad (Br7)$$

$$HOBr + h\nu \longrightarrow OH + Br \qquad (Br16)$$

$$\text{I net:} O_3 + HO_2 + h\nu \longrightarrow 2O_2 + OH$$

Uptake of HOBr is an alternative route for reaction (Br16) which cycles Br back to the gas phase. The simplest catalytic ozone production cycle is:

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2$$

$$HO_2 + NO \longrightarrow OH + NO_2$$

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 \longrightarrow O_3$$

$$\text{II net: } CO + 2O_2 + h\nu \longrightarrow CO_2 + O_3$$

This is being "shortcut" by cycle I which converts HO_2 back to OH without oxidizing NO to NO_2. The net effect on odd oxygen is therefore to destroy one molecule of O_x (=BrO) instead of producing one (=NO_2). Another "shortcut" occurs in the NO_x cycle:

$$BrO + NO \longrightarrow Br + NO_2 \qquad (Br9)$$

by oxidizing NO to NO_2 without changing the sum of odd oxygen (O_x) because both BrO and NO_2 are members of the O_x family (see also discussion in e.g. Stutz et al., 1999; Platt and Hönninger, 2003). The latter, however, does not lead to a change of the NO to NO_2 ratio on a global scale as explained in Sect. 3.4.

In this study we examine the potential effects of the presence of 0.5–2 pmol mol^{-1} of BrO on the photochemistry (mainly ozone and DMS) in the (free) troposphere and discuss where we should focus our future research in this field. We describe the model and the source scenarios that we used in Sect. 2 and will discuss the implications for tropospheric chemistry in Sect. 3 focussing on O_3, HO_x, NO_x, and DMS. In Sect. 4 we conclude and list future research needs.

2. Model description and source scenarios

We used the three-dimensional chemical transport model MATCH-MPIC (Lawrence et al., 1999; von Kuhlmann et al., 2003) for this study which includes a comprehensive treatment of tropospheric gas phase chemistry including non-methane hydrocarbons. We added reactions relevant for bromine processing and bromine-related ozone destruction and the oceanic sources of DMS after Kettle et al. (1999) and its destruction by OH, NO_3, BrO, and Br. The additional reactions are listed in Table 2. Wet and dry deposition is included as a function of the Henry's laws constant of the compounds.

The actual sources for the tropospheric inorganic bromine (Br_{inorg}) are still poorly constrained. They include downward transport from the stratosphere in mid to high latitudes, "spillout" and uplifting from polar surface ODEs, upward transport from the marine boundary layer, volcanoes, organohalogens (e.g. CH_3Br, CH_2Br_2, $CHBr_3$, and $CHBr_2Cl$) which are broken down by photolysis and/or reaction with OH, release of inorganic halogens by biomass burning as shown in laboratory experiments (Bill Keene, pers. comm.), or other, so far unidentified processes. Many of these sources will have a seasonal cycle which we do not take into account in this exploratory study. To sustain a tropospheric concentration of Br_{inorg} of about 7.5×10^7 molec cm^{-3} and assuming a

Br_{inorg} lifetime of 1–2 weeks in the FT a global source of 60–120 molec cm^{-3} s^{-1} or 5.6–11×10^{7} molec cm^{-2} s^{-1} would be needed. It is likely that the total source is actually composed of several of the aforementioned sources.

To reproduce the previously mentioned mixing ratios of BrO in the FT we tested four different hypothetical source scenarios (see Table 1): "tropics", "high lat", "constant", and "strat" which reflect different possible source types/regions, namely the tropics, high latitudes, a source constant with latitude, and only downward flux of inorganic bromine from the stratosphere plus photochemical breakdown of CH_3Br. We have chosen this set of model runs to study the variablities in the impacts related to different spatial distributions of BrO.

For the scenario "tropics" we used the simplified reaction:

$$Br_{org} + OH \longrightarrow Br + \text{products} \qquad \text{(Br20)}$$

with a generic organic bromine compound Br_{org} (with fixed mixing ratio of 300 pmol mol^{-1} Br) as bromine source, constituting a bromine source of about 100 molec cm^{-3} s^{-1} at a temperature of T=250K and an OH concentration of 10^{6} molec cm^{-3}. The OH dependence ensures a direct coupling with the photochemistry and makes this bromine source most important in the tropics where OH concentrations are highest.

The bromine source of the scenario "high lat" is independent of photochemistry and increasing with latitude, corresponding to a dominance of downward transport from the stratosphere and spillout from polar surface ODEs. We used $F_{\text{high lat}} = (15 + 0.5\phi)\frac{[M(\phi)]}{[M_0(\phi)]}$ molec cm^{-3}s^{-1}, where ϕ is the latitude in degrees and $[M]$ and $[M_0]$ the concentration of air molecules at current altitude and at the surface, respectively.

In the scenario "const" the source is also independent of photochemistry but constant with latitude, $F_{\text{const}} = (34 \text{ molec cm}^{-3}\text{s}^{-1})\frac{[M(\phi)]}{[M_0(\phi)]}$. In scenarios "high lat" and "const" no time dependence of the bromine source was assumed, whereas the dependence on [OH] in scenario "tropics" leads to a diurnally and seasonally varying bromine source.

The scaling with the concentration of air molecules in scenarios "high lat" and"const" ensures that the Br_{inorg} source is constant with altitude in mixing ratio (mol mol^{-1} s^{-1}) but obviously not in concentration (molec cm^{-3} s^{-1}). Due to different chemical regimes and washout rates the impact and lifetime and therefore "steady state" mixing ratio is different with altitude and with latitude.

The only bromine sources in scenario "strat" are downward flux of inorganic bromine from the stratosphere and decomposition of CH_3Br (with constant mixing ratio of 10 pmol mol^{-1}) in the troposphere by reaction with OH. To calculate the downward flux we used fixed concentrations of inorganic bromine in the stratosphere (dependent on latitude and season) as a boundary condition, the data are taken from a two-dimensional stratospheric model (Brühl et al., 1998; WMO, 2003). As explained by von Kuhlmann et al. (2003) a factor of 0.5 has to be used to properly simulate the stratosphere-troposphere exchange of O_3 in the model. In the scenario "strat" we applied the same ratio for the downward flux of inorganic bromine.

If only gas phase reactions are included, the cycling of HOBr, HBr, and $BrNO_3$ is rather slow and the resulting BrO concentrations are small. It was shown in many studies, however, that very efficient cycling of inorganic bromine occurs on and within aerosol particles (see e.g. overview by von Glasow and Crutzen, 2003, and references therein). Our simplified approach for the heterogeneous reactions is:

$$HOBr + HBr \xrightarrow{het} Br_2\ (+..) \qquad \text{(Br18)}$$

$$BrNO_3 \xrightarrow{het} HOBr\ (+..) \qquad \text{(Br19)}$$

based on detailed reaction cycles (Fan and Jacob, 1992; Abbatt, 1994; Vogt et al., 1996; Sander et al., 1999; Fickert et al., 1999). In the current model version no aqueous phase species are considered, therefore we listed only the gas phase products, other products are assumed to be taken up irreversibly by the aerosol. We used the approach of the reaction of HOBr with HBr on aerosol surfaces because of the high solubility of HBr, a possible enrichment of bromide on the aerosol surface (Jungwirth and Tobias, 2002), and the already mentioned high reaction probabilities on aerosols.

Note that reaction (Br19) constitutes loss of NO_x for the gas phase (see discussion in Sect. 3.4). We use the heterogeneous reaction rates as calculated by Dentener and Crutzen (1993) using a reaction probability of $\gamma = 0.1$ and taking gas phase diffusion limitations into account. To investigate the implications of bromine recycling on aerosol we repeated scenario "high lat" without aerosol recycling ("no recycling") and a 10 times faster recycling rate ($k'_{het} = 10. \times k_{het}(\gamma = 0.1)$) which approximately corresponds to $\gamma = 0.5$ for the size distribution chosen by Dentener and Crutzen (1993). Very high reaction probabilities of the involved bromine species have been observed on different substrates (Sander et al., 2003), and, as explained below, the results with faster heterogeneous reaction rates yield better agreement with the available information on BrO tropospheric vertical columns, therefore we used the higher recycling rate k'_{het} for all scenarios except for "high lat, no recycling" and "high lat, slow recycling".

Many details of the bromine recycling are still unknown, cycling of HOBr on frozen salt surfaces (Adams et al., 2002) or cirrus clouds, or in stratiform clouds (von Glasow et al., 2002a) are additional routes. If these bromine recycling reactions or other processes that reduce the loss of inorganic bromine are confirmed to be of importance, a smaller source for inorganic bromine would be needed to reproduce the reported BrO mixing ratios.

As already mentioned, the actual recycling of inorganic halogens on aerosols happens in a more complicated way but by using this approach we assume a dependence on the available aerosol surface area and yield BrO mixing ratios that are close to those deduced from satellite observations and balloon measurements (see Sect. 3.1). No aerosol components are transported in the current model version, so potential accumulation effects on the aerosol or a spatial redistribution of bromine by transport/settling of aerosol and time-delayed release of inorganic bromine from the aerosol cannot be simulated in this model version.

A model resolution of $11.25^\circ \times 11.25^\circ$ at the equator (T10) with 28 vertical levels is used. This is sufficiently high to examine the large scale features and the overall effects of bromine especially considering the uncertainties in the source strength and distribution. All scenarios were run for 12 months after a spinup of 16 months each.

3. Results

3.1. Br_{inorg} distributions

We start by briefly discussing the distribution of bromine species in the different scenarios before we explain the impacts of bromine on other trace gases. Total tropospheric Br_{inorg} levels in all scenarios are about 1–6 pmol mol^{-1} (see e.g. Fig. 6 for scenario "high lat") except for run "strat" where they are below 1 pmol mol^{-1}. In scenarios with a faster recycling rate compared to runs with slower or no recycling Br_{inorg} increases by more than 200% in regions with high wet deposition rates, i.e. the tropics but also in southern mid latitudes in altitudes of 900 to 500 hPa. Faster recycling implies higher $BrO : Br_{inorg}$ and $Br_2 : Br_{inorg}$ values and therefore less deposition as these two species are relatively insoluble. HBr and $BrNO_3$ (and HOBr), on the other hand, get washed out rapidly. In the "tropics" scenario Br_{inorg} mixing ratios in the tropics are up to 5 pmol mol^{-1} and only around 2 pmol mol^{-1} in high latitudes whereas in the case "high lat" they are less than 2 pmol mol^{-1} in the tropics and up to 5 pmol mol^{-1} in high latitudes. In the scenario "const" the numbers are similar to "high lat" with a smaller but discernable increase from the tropics to higher latitudes (see explanation below). In all scenarios Br_{inorg} mixing ratios increase with altitude (see below).

The zonally averaged annual mean mixing ratio of BrO (24 h average) is less than 0.5 pmol mol^{-1} in all scenarios for most of the troposphere and reaches 2 pmol mol^{-1} only in the upper troposphere especially in scenario "tropics" (see Figs. 1, 2, and 3). It increases with altitude and southern latitude. The BrO distribution in the "const" and "tropics" runs is latitudinally more uniform than that of case "high lat". This latitudinal pattern in the scenario "high lat" follows roughly the trend in Br_{inorg} but the zonally averaged ratio of BrO to Br_{inorg} (24 h average) also increases with altitude (in all runs) with values of 0.05 near the surface increasing to 0.3 at the top of the troposphere (see Fig. 7). This is mainly due to an increase in solar radiation and therefore shorter lifetimes of HOBr and $BrNO_3$. This trend is present in all scenarios but the increase with altitude is faster in runs with higher recycling rates. Another factor is the increase in Br_2:Br_{inorg} and a decrease in HOBr:Br_{inorg} with altitude which increases the relative contribution of BrO because the photolysis rate for Br_2 is greater than for HOBr and increases Br_{inorg} with altitude by a reduction in the washout of Br_{inorg} because of differences in solubility of Br_2 and HOBr.

It has been shown with a one-dimensional model (von Glasow et al., 2002b) that the difference of the wavelength dependence of $O_3 \longrightarrow O(^1D)$ and Br_2 photolysis leads to a diurnal variation of BrO with small morning and afternoon peaks if HO_2 is the main sink, and a broad diurnal variation with a small peak at noon if NO_2 is the main sink. These two types of diurnal variations are found in our 3D model results as well.

Figurs 4 and 5 show the vertically integrated tropospheric column density (using the WMO definition of the tropopause) of BrO for the scenarios "high lat" and "tropics", respectively, with values of about $0.5–1\times10^{13}$ molec cm^{-2} in the tropics and up to 2.4×10^{13} molec cm^{-2} in higher latitudes. The large gradient in the tropopause height in the subtropics leads to a maximum in the vertical column of BrO in that region. The maximum values are reached only in the subtropics, in most parts of the troposphere these model BrO vertical columns are somewhat smaller than the tropospheric vertical BrO columns of $<$1-3$\times10^{13}$ molec cm^{-2} that were derived from comparisons of satellite, balloon, and ground measurements (Pundt et al., 2000; Van Roozendael et al., 2002; Richter et al., 2002), therefore the results presented here should be regarded as a conservative estimate of the overall effects of bromine chemistry in the troposphere.

The inorganic bromine levels in scenario "strat" are by far too small to explain the observed tropospheric vertical columns which in this run are only $0.5–2\times10^{12}$ molec cm^{-2}. The annually and zonally averaged 24 h mixing ratios of BrO are less then 0.25 pmol mol^{-1} in the troposphere (see Fig. 3). This implies that downward flux of stratospheric inorganic bromine and decomposition of CH_3Br are not sufficient and additional sources of reactive bromine have to be active.

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3.2. Effect on ozone

The runs with bromine levels that reproduce the observations best lead to a notable decrease in O_3. Even in the runs with smallest BrO mixing ratios of only a few tenth of a pmol mol^{-1} (scenario "high lat, no recycling" and "strat") the annually and zonally averaged difference to the run without bromine chemistry is of the order of several percent. In the case "high lat, slow recycling" with higher BrO mixing ratios it is already 5–10% throughout the troposphere, whereas in the run with BrO mixing ratios that are closest to the values deduced from satellite and balloon observations ("high lat") the difference in zonal mean O_3 mixing ratio compared to the run without bromine chemistry is 6–18% (see Fig. 8). Maximum local differences are up to 40% in the austral summer high latitudes. These numbers imply that there might be an important O_3 destruction mechanism in the troposphere that has been neglected so far.

Even though the mixing ratio and distribution of Br_{inorg} and BrO differ among the different scenarios, the overall vertical and latitudinal distribution of the effect on O_3 remains similar in all discussed runs, namely that O_3 destruction is strongest in the FT of the southern hemisphere. It is smallest near the ground in northern mid latitudes. This is due to smaller sensitivities of the photochemistry to perturbations when high O_3 sources and sinks are present as is the case in the polluted regions compared to a greater sensitivity in the more pristine FT in the southern hemisphere where photochemical sources and sinks for O_3 are smaller. In scenario "tropics" the maximum of the difference in zonally averaged O_3 (up to 20% less O_3 compared to a run without bromine chemistry) is shifted from higher latitudes towards 50–30° S and strongest in magnitude compared to all presented cases. Nevertheless, even in this case the main pattern with highest differences in O_3 in the southern FT remains the same.

Compared to the run without bromine chemistry, the tropospheric burden of O_3 (see Table 3) is reduced in scenarios "high lat", "tropics", and "strat" by 10%, 15%, and 3%, respectively. The ozone loss by reaction (Br7) equals approximately 28% of the dry deposition in run "high lat".

3.3. Effect on HO_x

The reaction $BrO + HO_2 \longrightarrow HOBr$ destroys HO_2 and the subsequent photolysis of HOBr releases OH. Both processes are acting in the direction of an increase in the OH to HO_2 ratio. This shift is highest in the upper FT with up to 50% and 40% in the southern and northern high latitudes, respectively, in the scenario "high lat" (compared to the ratio in the run without bromine, see Fig. 11). In mid and low latitudes this effect is less than 10%. As mentioned in the introduction, this shift implies less O_3 production because in the reactions

$$BrO + HO_2 \longrightarrow HOBr + O_2 \qquad \text{(Br7)}$$

$$HOBr + h\nu \longrightarrow OH + Br \qquad \text{(Br16)}$$

HO_2 gets cycled back to OH without oxidizing NO to NO_2. Furthermore reaction Br7 destroys O_x because BrO is part of the odd oxygen family. The decrease in HO_2 concentrations compared to scenario "no hal" is up to 10% in runs "high lat" and "tropics" with the strongest effect in the free troposphere. In the run "high lat" it is most pronounced at high latitudes whereas it is more uniform with latitude in the run "tropics".

The OH concentration increases in the upper FT by more than 20% compared to the run without bromine chemistry but this is contrasted by small relative decreases in OH in the tropics. Most OH, however, is located in the tropics where the reduction in O_3 is strong enough to reduce OH, so that the change in global mean OH concentrations (calculated weighted with CH_4 as well as with air mass after Lawrence et al., 2001) is only for the "tropics" scenario on the order of 1–2%. For the other runs it is virtually indiscernible from scenario "no hal". The lifetime of CH_4 is almost unchanged compared to "no hal" in all runs but "tropics" where it increased from 9.62 years to 9.83 years, again only 2% so that these effects are negligible.

H_2O_2 decreases with latitude and altitude compared to the run without bromine chemistry (see Fig. 12). This is caused by the decrease in HO_2 which is the main precursor for H_2O_2. The decrease in H_2O_2 in the tropics is a few percent in scenario

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“high lat” and 5–10% in scenario “tropics” but more than 20% in the high latitude free troposphere. The reduction is therefore larger than that in HO_2, because the formation rate of H_2O_2 in reaction

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

is quadratic in HO_2. The decrease in H_2O_2 can be of importance for atmospheric chemistry because the gas phase is the main source for aqueous H_2O_2 which is the most important oxidant for S(IV) to S(VI) in the aqueous phase. A reduction in H_2O_2 would reduce the formation rates of particulate sulfate which however is likely to be compensated by HOBr (and HOCl) as aqueous phase oxidants as explained e.g. in von Glasow and Crutzen (2004).

3.4. Effect on nitrogen oxides

The runs including bromine chemistry also lead to changes in the NO_x mixing ratios in mid and high latitudes and especially in the FT. In the scenario “high lat” NO_x concentrations are up to 25% smaller than in the run without bromine chemistry. In the lower troposphere, especially in the tropics, NO_x increases by a few percent. These changes are approximately correlated with changes in HO_2 and anticorrelated with changes in peroxy acetyl nitrate (PAN) and OH. This is caused by an increase in the formation of PAN from the peroxy acetyl (PA) radical which is caused by a decrease in HO_2 that destroys PA.

A decrease in NO_x concentrations reduces the photochemical production of O_3. This highlights that the difference in O_3 in our model runs is a combination of increased O_3 destruction by bromine and reduced O_3 production due to less NO_x (indirectly caused by bromine) stressing the importance to consider all elements of the chemical system.

As already mentioned in the introduction, the reaction $BrO + NO \longrightarrow Br + NO_2$ reduces the production rate of O_3 by oxidizing NO to NO_2 without changing the sum of odd oxygen. In the model results, however, the ratio of NO to NO_2 decreases only in the uppermost troposphere in high latitudes and in the stratosphere. In most of the

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troposphere the ratio increases compared to a run without bromine chemistry. (see Fig. 13). This is caused by decreases in the O_3 and HO_2 concentrations which are crucial for the steady state ratio of NO to NO_2 and which cannot be compensated by the presence of less than 2 pmol mol^{-1} BrO (see e.g. Brasseur et al., 1999):

$$\frac{[NO]}{[NO_2]}=J(NO_2)\times\left(k_{NO+O_3}[O_3]+k_{HO_2+NO}[HO_2]+k_{CH_3O_2+NO}[CH_3O_2]+k_{BrO+NO}[BrO]\right)^{-1} \quad (1)$$

The ratio of $BrNO_3$ to Br_x is highest in northern mid latitudes near the ground, the highest $BrNO_3$ mixing ratios are found near the tropopause, they are less than 0.5 pmol mol^{-1} in most of troposphere in all runs except for "tropics" where they can reach up to 1 pmol mol^{-1} in the tropical mid troposphere. The heterogenous reaction of $BrNO_3$ produces particulate NO_3^- (see Sander et al., 1999) and therefore contributes to the loss of NO_x. This NO_x loss by the heterogeneous reaction of $BrNO_3$ is about 4.5 and 10% of the NO_x loss by reaction NO_2 + OH $\longrightarrow$ HNO_3 in the runs "high lat" and "tropics", respectively.

3.5. Effect on DMS

Another very significant result of our study is the impact of BrO on DMS chemistry with a strong reduction of its mixing ratio and a drastic change in its oxidation pathways. DMS is emitted by marine organisms and is the main natural source for reactive sulfur in the marine atmosphere. The main sinks of DMS are usually thought to be reaction with OH and NO_3, however, the reaction of DMS with BrO can be a significant sink as well (Toumi, 1994). In the cloudy MBL an increase in DMS oxidation by BrO leads to the production of more DMSO which is rapidly taken up by clouds. This reduces the DMS to SO_2 conversion efficiency, which is indicative of the potential for formation of new cloud condensation nuclei (CCN), but increases the size of already present CCN by the formation of particulate sulfur (methyl sulfonic acid and sulfate) (von Glasow et al., 2002a; von Glasow and Crutzen, 2004). This and other feedbacks like increased drizzle formation due to larger CCN would lead to a reduction in cloud albedo. Boucher et al. (2003) performed a sensitivity study with a global model assuming a constant daytime BrO mixing ratio of 1 pmol mol^{-1} in the MBL and found a reduction of the tropospheric DMS burden by about 30%. In our model runs the tropospheric DMS burden is reduced by 26%, 23%, and 6% in scenarios “high lat”, “tropics”, respectively (see Table 3).

The vertical columns of DMS mixing ratios (dominated by the MBL) are reduced by 3–30% in run “high lat, no recycling” with the smaller values close to the equator. In runs “high lat” and “tropics” the difference to “no hal” in many regions is more than 10%, and it is especially high in the regions with highest DMS fluxes and mixing ratios, the Southern Ocean (Kettle et al., 1999) as evident from Figs. 14 and 15. The spatial distribution of the DMS differences in the model is caused by a latitudinal gradient in BrO with annually averaged 24 h mean mixing ratios in the boundary layer of 0.05 (0.4) pmol mol^{-1} in the tropics and 0.3 (0.1) pmol mol^{-1} in high latitudes for scenario “high lat (“tropics”). Note that DMS mixing ratios are highest in the MBL where our bromine source approach will likely underestimate BrO mixing ratios because we did not include expolicitly sea salt aerosol as a source.

The main difference of our study to that by Boucher et al. (2003) is, that they assumed a constant daytime BrO mixing ratio of 1 pmol mol^{-1} everywhere in the MBL whereas in our model runs the 24 h average mixing ratio of BrO in the MBL is only 0.1–0.3 pmol mol^{-1} in “high lat” and less than 0.05 pmol mol^{-1} in runs “high lat, no recycling” and “strat”.

The previously discussed increases in DMS oxidation, the shift in its oxidation products, and the changes in resulting new partcile formation and growth of existing aerosol particles have the potential to dramatically alter our understanding of the DMS – CCN – climate connection. Moreover, some estimates of the DMS flux from the ocean rely on a comparison with atmospheric models to calculate the photochemical loss rate of DMS without taking oxidation by BrO into account, implying that DMS fluxes from these studies might be underestimating the real fluxes.

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4. Conclusions and future research needs

Our results show that even low levels of reactive bromine can greatly disturb tropospheric chemistry affecting not only ozone but also HO_x, NO_x, and sulfur.

While there is a substantial body of evidence for the presence of relevant levels of tropospheric BrO we have to support this with more direct and indirect measurements in all parts of the troposphere. In our model the widespread impact of bromine on tropospheric chemistry is caused by BrO mixing ratios that are around the detection limit of current instruments. For these reasons it is highly desirable to improve the detection limits, especially the sensitivity of space-borne instruments to BrO in the MBL to yield global coverage.

A first step to improve our knowledge about the global distribution of reactive bromine in the troposphere would be to conduct airborne studies in the free troposphere to check whether BrO is present at lower latitudes as well or if it is confined to high latitudes where it could already be measured.

We want to stress that we did not include any short-lived organohalogens or sea salt derived bromine in the MBL which would potentially lead to higher BrO mixing ratios in the MBL especially increasing the impact on DMS. An additional focus of future research in this field should be to investigate the contribution, spatial and temporal distribution of the different sources to global tropospheric bromine levels.

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Table 1. Overview of scenarios used in this study.

scenario	heterogeneous reactions	description
high lat	$k'_{het} = 10. \times k_{het}(\gamma = 0.1)$ [a]	Br source increases with latitude
high lat, slow recyc.	$\gamma = 0.1$	Br source increases with latitude
high lat, no recyc.	off	Br source increases with latitude
const	$k'_{het} = 10. \times k_{het}(\gamma = 0.1)$ [a]	Br source constant with latitude
tropics	$k'_{het} = 10. \times k_{het}(\gamma = 0.1)$ [a]	Br source decreases with latitude
strat	$k'_{het} = 10. \times k_{het}(\gamma = 0.1)$ [a]	Br downward transport from stratosphere plus decomposition of CH_3Br
nohal	$k_{het} = 10. \times k_{het}(\gamma = 0.1)$ [a]	no bromine

[a]: see explanation in text, the effective gamma for these runs is approx. $\gamma = 0.5$.

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Table 2. Bromine reactions.

no	reaction	n	A [(cm^{-3})$^{1-n}$s^{-1}]	$-E_a$ / R [K]	reference
Br 1	$Br + O_3 \longrightarrow BrO + O_2$	2	1.7 $\times 10^{-11}$	-800	Sander et al. (2003)
Br 2	$Br + HO_2 \longrightarrow HBr + O_2$	2	1.5 $\times 10^{-11}$	-600	Sander et al. (2003)
Br 3	$Br + C_2H_4 \xrightarrow{O_2} HBr + C_2H_5O_2$	2	5. $\times 10^{-14}$		Singh and Zimmerman (1992)
Br 4	$Br + HCHO \xrightarrow{O_2} HBr + CO + HO_2$	2	1.7 $\times 10^{-11}$	-800	Sander et al. (2003)
Br 5	$Br + CH_3OOH \longrightarrow CH_3OO + HBr$	2	2.66 $\times 10^{-12}$	-1610	Mallard et al. (1993)
Br 6	$Br + BrNO_3 \longrightarrow Br_2 + NO_3$	2	4.9 $\times 10^{-11}$		Orlando and Tyndall (1996)
Br 7	$BrO + HO_2 \longrightarrow HOBr + O_2$	2	3.4 $\times 10^{-12}$	540	Sander et al. (2003)
Br 8	$BrO + CH_3OO \longrightarrow 0.72\ HOBr + 0.28\ Br + 0.28\ HO_2 + HCHO$	2	^{a} 5.7 $\times 10^{-12}$		Aranda et al. (1997)
Br 9	$BrO + NO \longrightarrow Br + NO_2$	2	8.8 $\times 10^{-12}$	260	Sander et al. (2003)
Br 10	$BrO + NO_2 \xrightarrow{M} BrNO_3$	2	^{b}		Sander et al. (2003)
Br 11	$BrO + BrO \longrightarrow 1.62\ Br + 0.19\ Br_2 + O_2$	2	2.95 $\times 10^{-12}$	40	based on Sander et al. (2003), 2 channels (different T-dependence) combined
Br 12	$HBr + OH \longrightarrow Br + H_2O$	2	1.1 $\times 10^{-11}$		Sander et al. (2003)
Br 13	$BrNO_3 \longrightarrow BrO + NO_2$	1	^{b}		Orlando and Tyndall (1996)
Br 14	$BrO + h\nu \xrightarrow{O_2} Br + O_3$	1	^{c}		DeMore et al. (1997)
Br 15	$Br_2 + h\nu \longrightarrow 2\ Br$	1	^{c}		Hubinger and Nee (1995)
Br 16	$HOBr + h\nu \longrightarrow Br + OH$	1	^{c}		Ingham et al. (1999)
Br 17	$BrNO_3 + h\nu \longrightarrow Br + NO_3$	1	^{c}		DeMore et al. (1997)
Br 18	$HOBr + HBr \xrightarrow{het} Br_2$ (+ ..)	2	^{4}		
Br 19	$BrNO_3 \xrightarrow{het} HOBr$ (+ ..)	1	^{4}		
Br 20	$Br_{org} + OH \longrightarrow Br$ (+ ..)	2	1.7 $\times 10^{-12}$	-1215	assumed, only for “tropics”, [Br_{org}]=300 pmol mol^{-1}
Br 21	$CH_3Br + OH \longrightarrow Br$ (+ ..)	2	1.7 $\times 10^{-12}$	-1215	Atkinson et al. (2003), only for “strat”
S1	$DMS + OH \xrightarrow{O_3} \{CH_3SO2 +\}\ HCHO$	2	1.12 $\times 10^{-11}$	-253.	
S2	$DMS + OH \longrightarrow \{0.5xDMSO + 0.5SO_2+\} + 0.5\ HO_2 + CH_3OO$	2			
S3	$DMS + NO_3 \xrightarrow{O_3} \{CH_3SO_2 +\}\ HNO_3 + HCHO$	2	1.9 $\times 10^{-13}$	520.	JPL 97
S4	$DMS + Br \xrightarrow{O_3} \{CH_3SO_2 +\}\ HBr + HCHO$	2	9.0 $\times 10^{-11}$	-2386	Sander et al. (2003)
S5	$DMS + BrO \longrightarrow \{DMSO +\}\ Br$	2	2.54 $\times 10^{-14}$	850	

n is the order of the reaction. ^{a} two reactions combined, ^{b} photolysis rates calculated online, ^{c} special rate functions (pressure dependent), ^{4} see text for explanation. The rate coefficients are calculated with $k = A \times \exp(\frac{-E_a}{RT})$. Note that the breakdown products of DMS are ignored in the model.

Table 3. Tropospheric burdens of O_3 and DMS in Tg.

scenario	O_3 burden	DMS burden
high lat	157.0	4.612
tropics	147.5	4.787
strat	172.2	5.848
nohal	174.6	6.249

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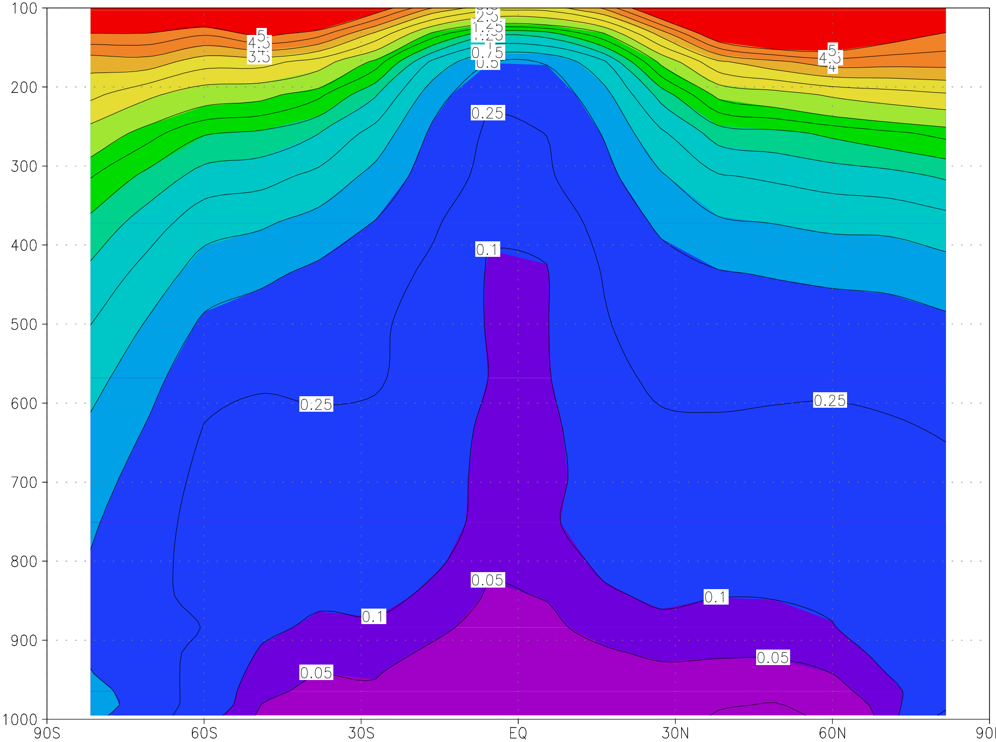

Fig. 1. Zonally and annually averaged mean of the BrO mixing ratio (in pmol mol^{-1}) for the scenario “high lat”. The ordinate is the pressure in hPa and the abscissa is latitude in degrees. Note that 24 h averages are plotted.

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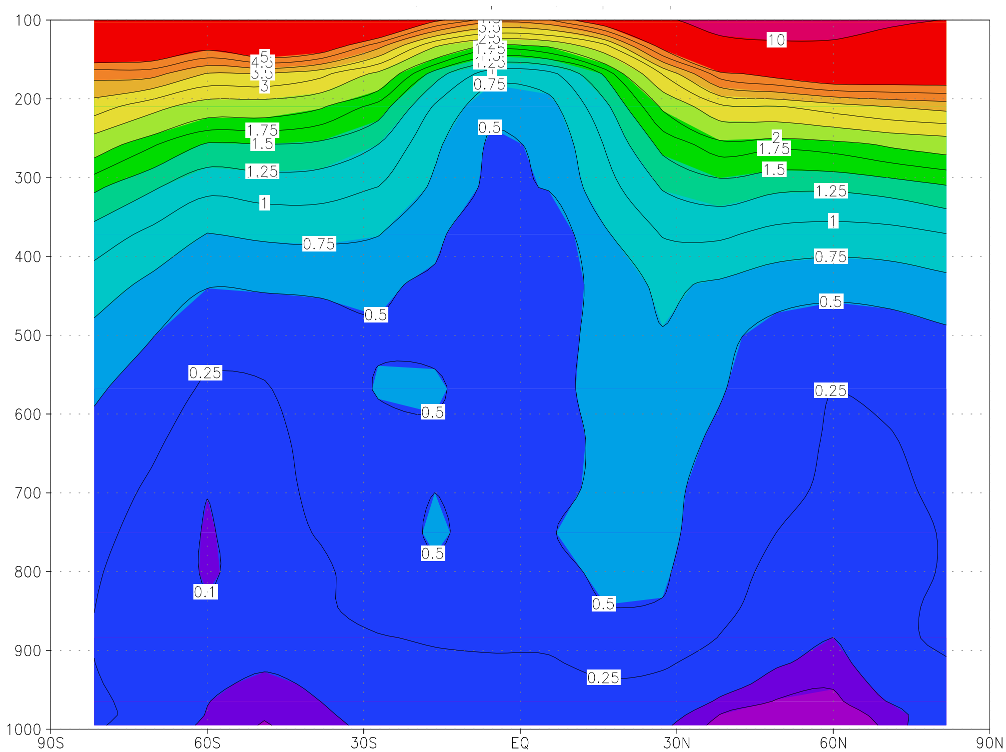

Fig. 2. As Fig. 1 but for scenario "tropics".

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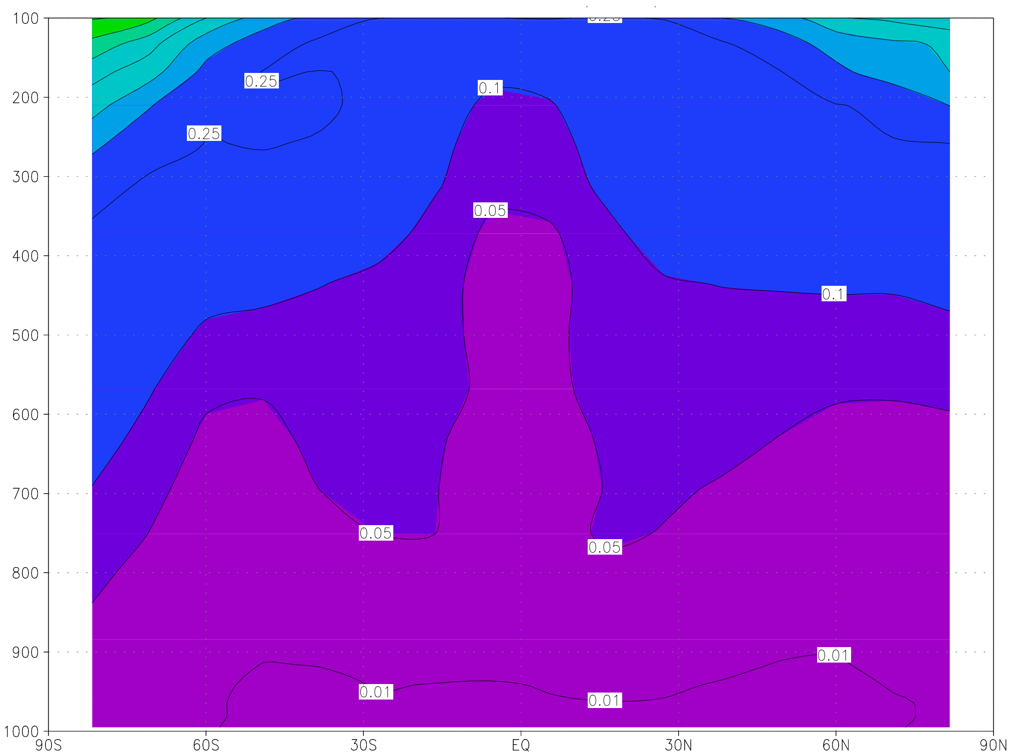

Fig. 3. As Fig. 1 but for scenario “strat”.

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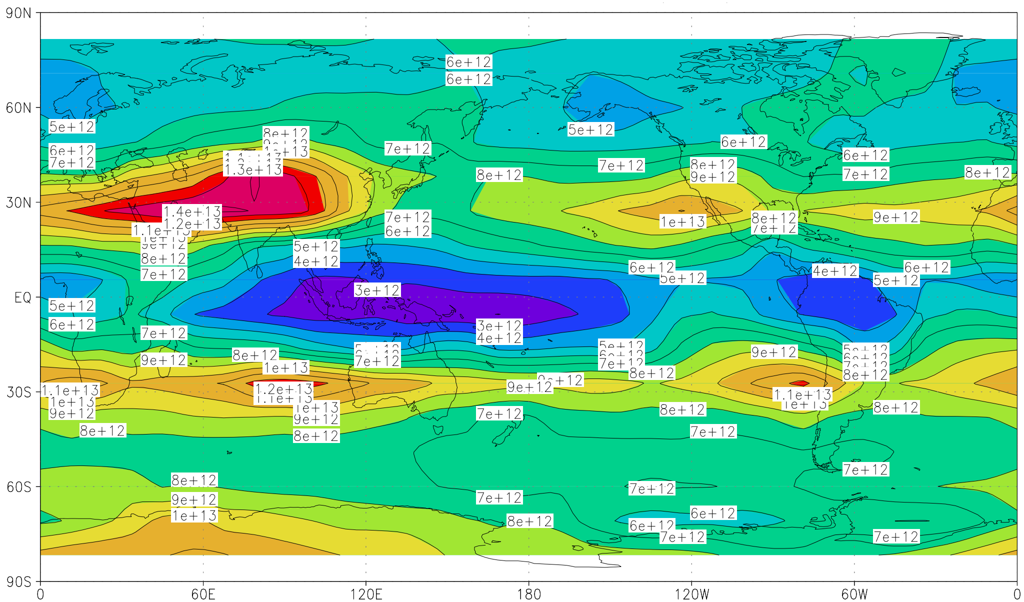

Fig. 4. Annually averaged tropospheric vertical column of BrO (in molec cm^{-2}) for the scenario “high lat”. We used the WMO definition for the determination of the tropopause. Note that 24 h averages are plotted. The ordinate is latitude in degrees and the abscissa is longitutde in degrees.

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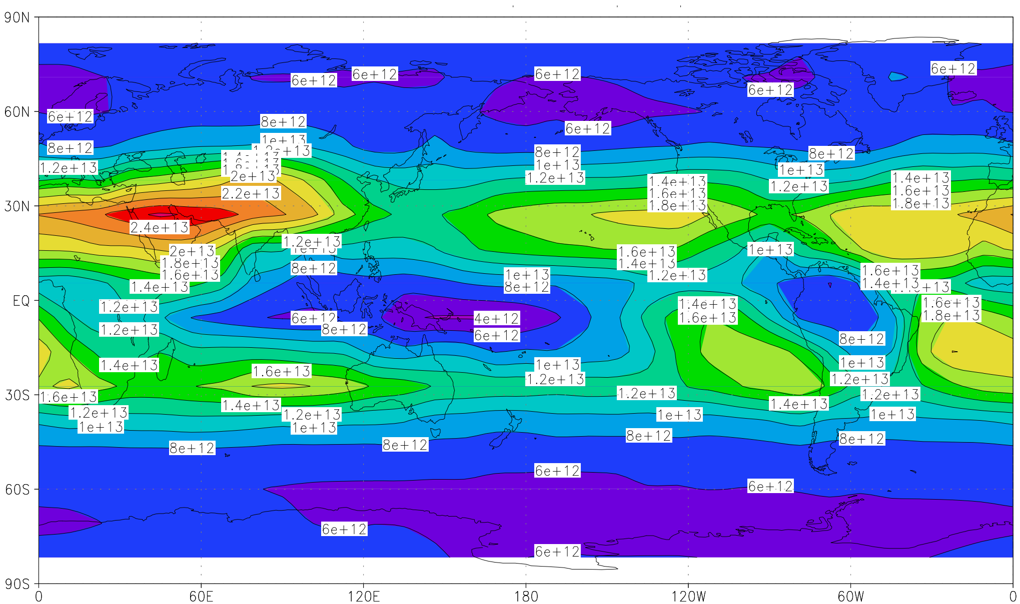

Fig. 5. As Fig. 4 but for scenario “tropics”.

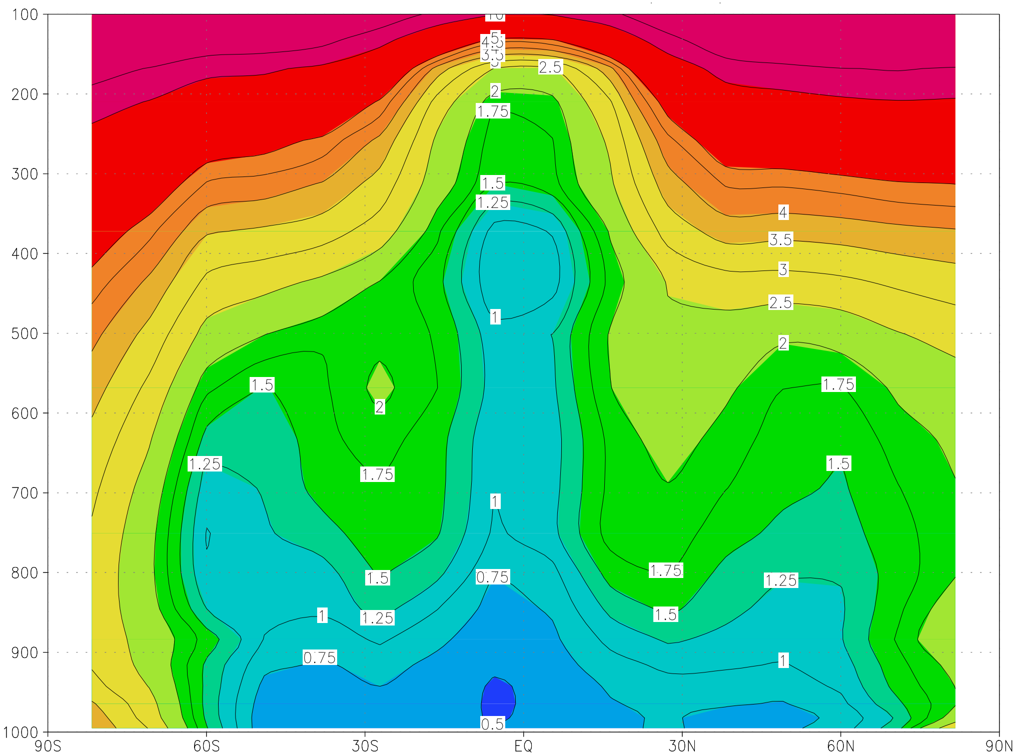

Fig. 6. As Fig. 1 but for Br_{inorg}.

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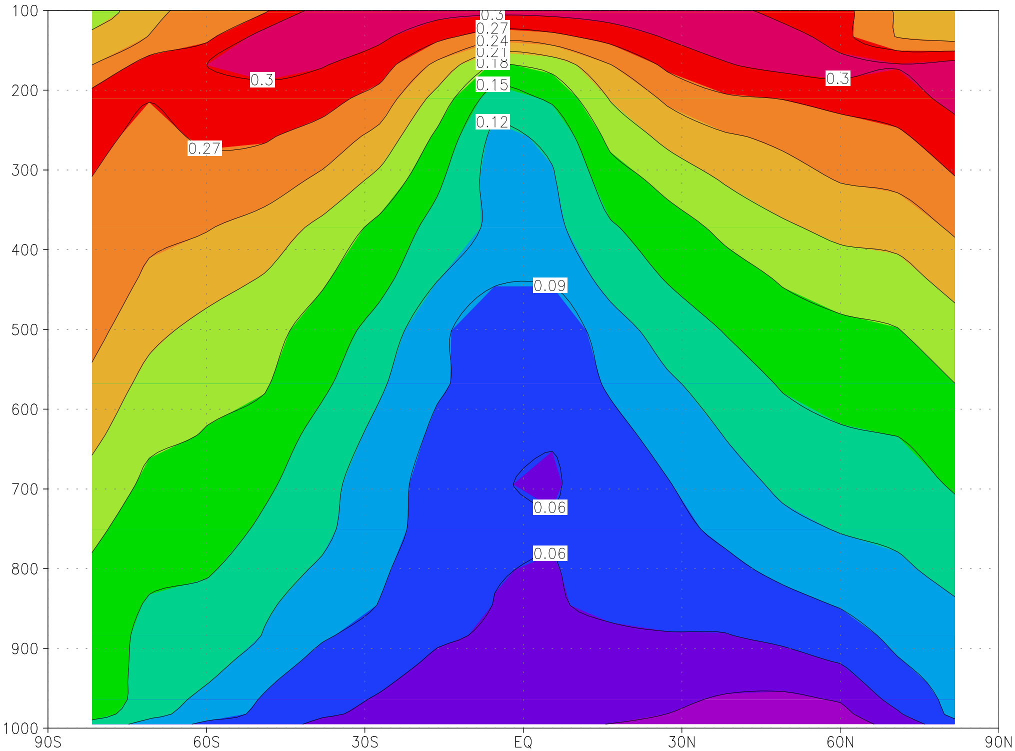

Fig. 7. As Fig. 1 but for the ratio of BrO to Br_{inorg}.

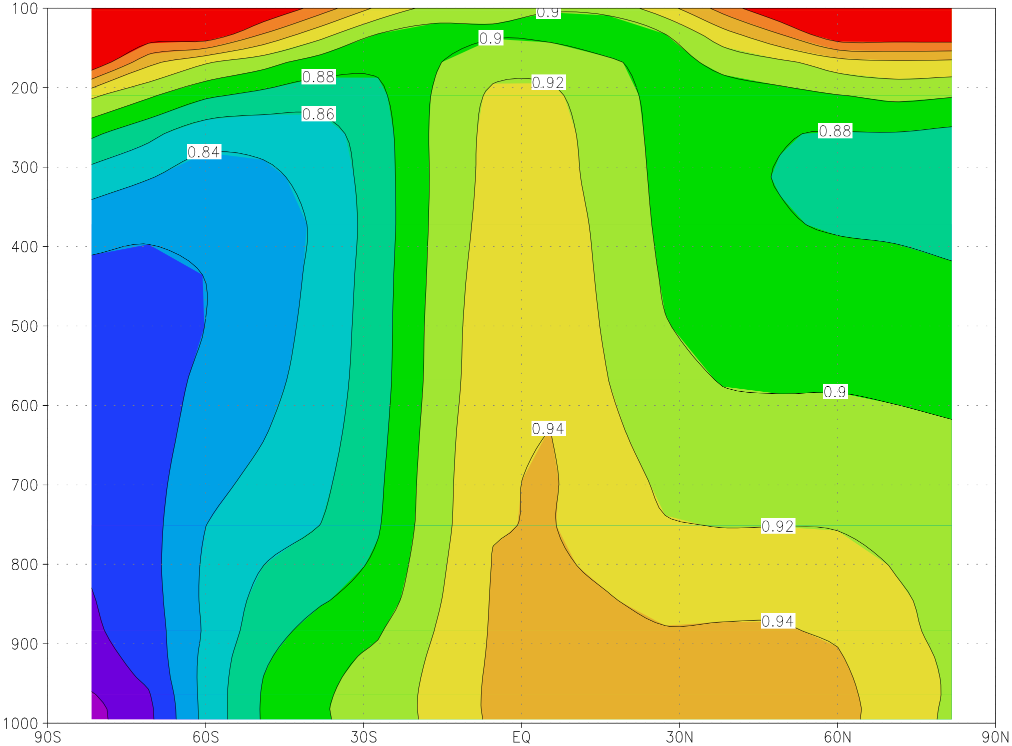

Fig. 8. Ratio of O_3 in scenario "high lat" to O_3 in scenario "no hal". The numbers are zonally and annually averaged. The ordinate is the pressure in hPa and the abscissa is latitude in degrees. Note that 24 h averages are plotted.

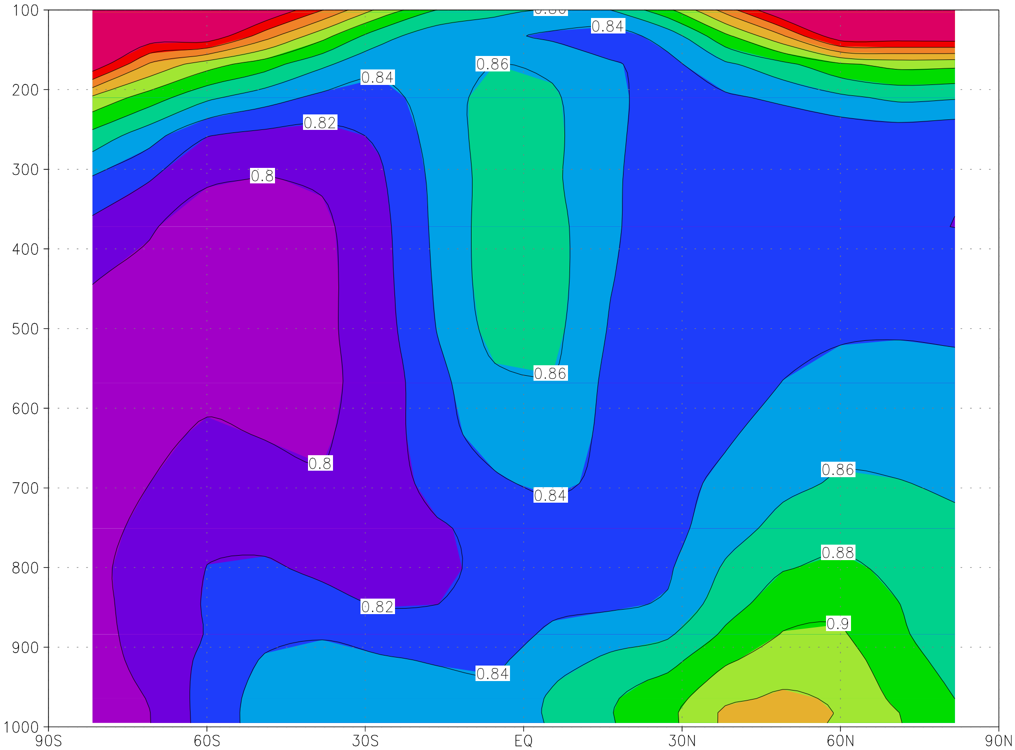

Fig. 9. As Fig. 8 but for the ratio of O_3 in scenario "tropics" to O_3 in scenario "no hal".

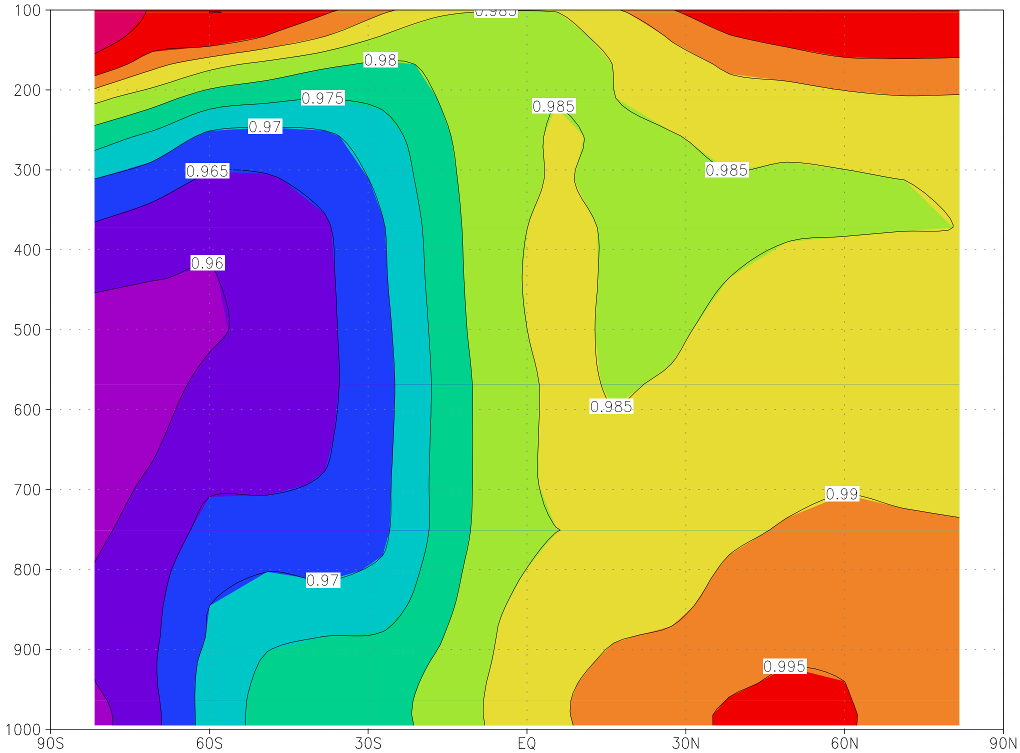

Fig. 10. As Fig. 8 but for the ratio of O_3 in scenario "strat" to O_3 in scenario "no hal".

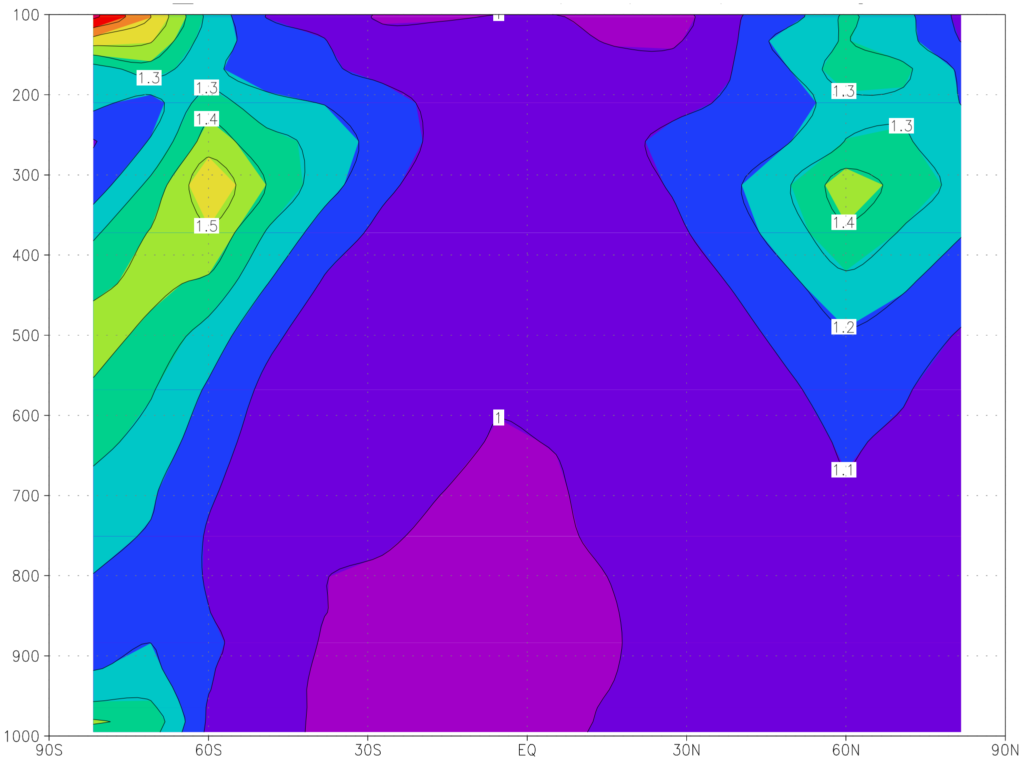

Fig. 11. As Fig. 8 but for the ratio of $OH:HO_2$ in scenario "high lat" to $OH:HO_2$ in scenario "no hal".

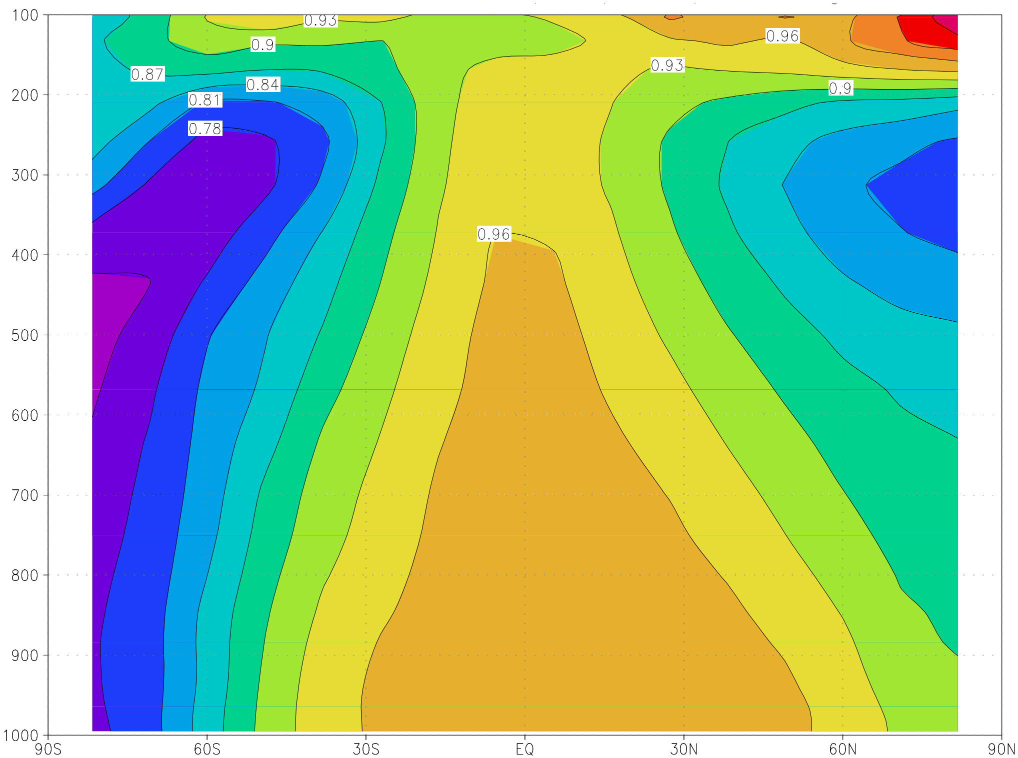

Fig. 12. As Fig. 8 but for the H_2O_2 in scenario "high lat" compared to $OH:HO_2$ in scenario "no hal".

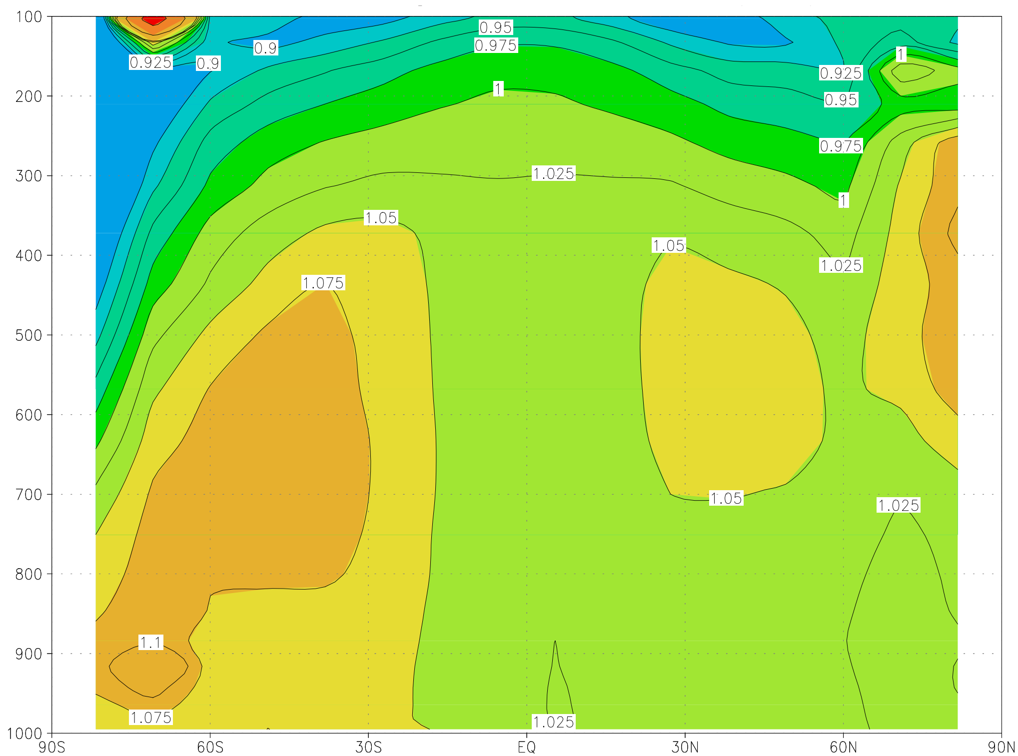

Fig. 13. As Fig. 8 but for the ratio of NO:NO_2.

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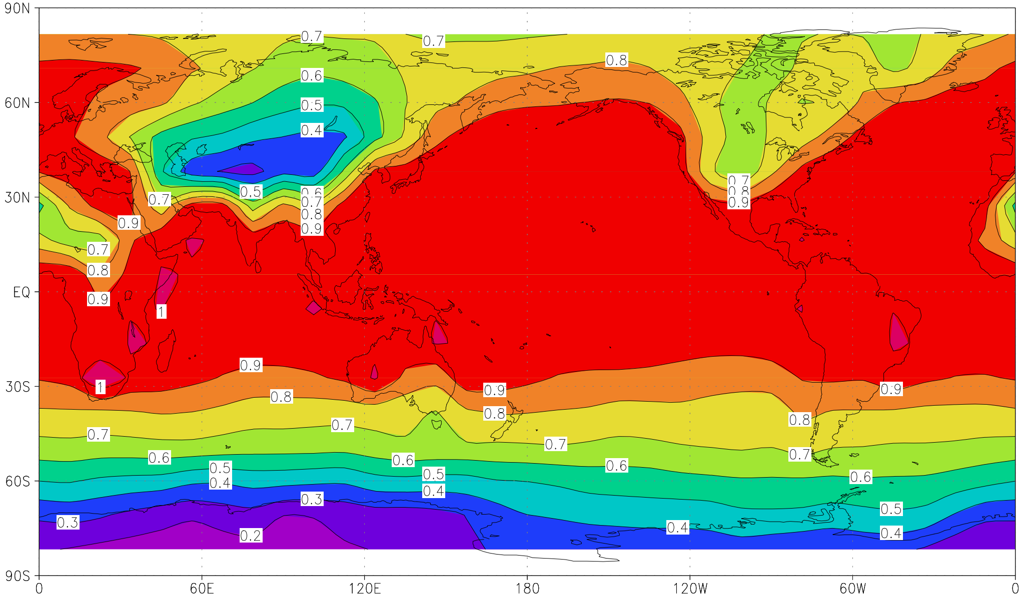

Fig. 14. Ratio of the vertical column of DMS for the scenario "high lat" to scenario "no hal" (annually averaged). The ordinate is latitude in degrees and the abscissa is longitutde in degrees.

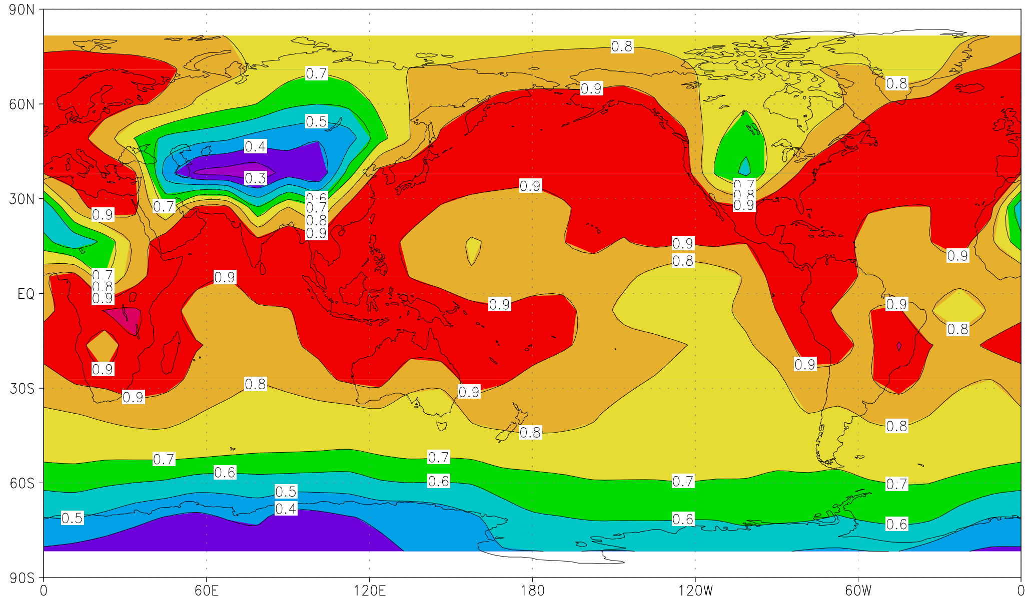

Fig. 15. As Fig. 14 but for scenario "tropics".

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